

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-119343

(43)Date of publication of application : 23.04.2003

(51)Int.Cl.

C08L 53/02
B29C 41/18
C08L 75/00
C08L 91/00
// B29K 55:02
B29K 75:00

(21)Application number : 2001-314945

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(22)Date of filing : 12.10.2001

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(54) POWDERY POLYMER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a powdery polymer composition containing a thermoplastic elastomer as a base, having excellent moldability and melt fluidity, effectively usable for powder forming such as slush molding and powder coating and giving a molded article or a coated product having excellent scratch resistance, abrasion resistance, softness, low-temperature characteristics, rubber elasticity, touch and appearance.

SOLUTION: The powdery polymer composition has an average particle diameter of $\leq 800 \mu\text{m}$ and is composed of (I) 100 pts.mass of an addition-polymerized block copolymer composed of (i) a block copolymer and/or its hydrogenated product having (A1) a polymer block composed mainly of an aromatic vinyl compound and (B1) a polymer block composed mainly of a conjugated diene compound, (II) 5-200 pts.mass of a polyurethane-based block copolymer having (C) an addition-polymerized block composed of (ii) a block copolymer or its hydrogenated product having (A2) a polymer block composed mainly of an aromatic vinyl compound and (B2) a polymer block composed mainly of a conjugated diene compound and (D) a thermoplastic polyurethane elastomer block, (III) 50-500 pts.mass of (iii) a thermoplastic polyurethane elastomer and (IV) 10-300 pts.mass of (iv) a softening agent.

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CLAIMS

[Claim(s)]

[Claim 1](i) As opposed to at least one sort of addition condensation system block copolymer (I) 100 mass parts chosen from a block copolymer which has a polymeric block (A1) which mainly consists of an aromatic vinyl compound, and a polymeric block (B1) which mainly consists of conjugated diene compounds, and its hydrogenation thing;

It is five to 200 mass part about polyurethane system block copolymer (II) characterized by comprising the following.;

(ii) An addition condensation system block (C) which consists of a block copolymer which has a polymeric block (A2) which mainly consists of an aromatic vinyl compound, and a polymeric block (B-2) which mainly consists of conjugated diene compounds, or its hydrogenation thing.

A thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D).

(iii) It is thermoplastic polyurethane elastomer (III) 50 to 500 mass part,; and (iv) A powdered polymer composition which consists of a thermoplastic polymer composition which contains softener (IV) at a rate of 10 - 300 mass-part,; and is characterized by mean particle diameter being 800 micrometers or less.

[Claim 2]The powdered polymer composition according to claim 1 whose melt flow rates (MFR) measured under a condition of temperature of 230 ** and 2.16 kg of load according to JIS K-7210 are 10g/10 minutes or more.

[Claim 3]The powdered polymer composition according to claim 1 or 2 which is an object for slush molding.

[Claim 4]A slush molding object which uses a powdered polymer composition of a statement for any 1 paragraph of claims 1-3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the slush molding object which uses a powdered polymer composition and this powdered polymer composition. In details, more this invention Slush molding, compression molding, powder thermal spraying, rotational casting, In the forming technique and paint art which are performed using powder, such as extrusion molding, calender molding, and various powder coating, can use conveniently, and by those shaping and paint. It is related with the slush molding object which consists of a powdered polymer composition which can manufacture the Plastic solid which is excellent in a sex with a crack-proof, and abrasion resistance, and is moreover excellent in pliability, dynamic strength, the low-temperature characteristic, and rubber elasticity, and a coat, and this powdered polymer composition.

[0002]

[Description of the Prior Art]The skin material which uses an elastic polyvinyl-chloride-resin constituent, It is cheap, and since it excels in pliability and a sex with a crack-proof, it is used from the former in a wide range of fields, such as furniture, such as automotive interior materials, such as an instrument panel, a door trim, a console box, and a seat, a sofa, and a chair. However, polyvinyl chloride resin has the doubt on which the plasticizer which generates toxic substances, such as dioxin, at the time of incineration, and is used there acts as environmental hormone, a carcinogenic substance, etc., and there is a problem in respect of environmental pollution or safety. Therefore, using the thermoplastic elastomer which contains neither halogen nor a plasticizer instead of polyvinyl chloride resin is examined in recent years. Although the slush molding which a powdered polyvinyl-chloride-resin constituent is made to adhere to the metallic mold surface which has complicated shape conventionally in manufacture of the especially above-mentioned skin material, and carries out hot forming has been used widely, Since there is a problem in respect of environmental pollution or safety as use of polyvinyl chloride resin was described above, the powdered thermoplastic elastomer composition in which slush molding is possible is proposed.

[0003]For example, to JP,10-182900,A. Polypropylene resin, hydrogenation (hydrogenation) styrene butadiene rubber, process oil, and the thermoplastic elastomer composition for powder slush molding containing oil-absorption-property elastomers (a styrene thermoplastic elastomer, thermoplastic elastomer olefin, etc.) are indicated. However, the thermoplastic elastomer composition for powder slush molding indicated in this gazette, Although an improvement is found in slush molding nature, the pliability of the Plastic solid acquired, rubber elasticity, dynamic strength, the low-temperature characteristic, a sex with a crack-proof, and in respect of abrasion resistance, it is not enough satisfactory.

[0004]To JP,10-279738,A, the powdered thermoplastic elastomer composition containing a styrene thermoplastic elastomer, two sorts of the ethylene and the alpha olefin copolymers in which densities differ, and crystal polypropylene resin is indicated. However, it is difficult to make a sex with a crack-proof and abrasion resistance, pliability and rubber elasticity, and a hand have with sufficient balance in the Plastic solids (slush molding object etc.) acquired from this powdered thermoplastic elastomer composition. That is, if pliability and rubber elasticity tend to

fall and a hand tends to become poor, when it is going to raise a sex with a crack-proof, and abrasion resistance, and it is, on the other hand, going to raise pliability, rubber elasticity, and a hand, a sex with a crack-proof and abrasion resistance will fail.

[0005]To JP,2000-302918,A. The thermoplastic elastomer composition for slush molding containing hydrogenation styrene butadiene random copolymer rubber, crystalline polypropylene resin, an internal release agent, an oil-absorption-property elastomer, process oil, and amorphous polypropylene resin is indicated. However, the slush molding object acquired using the thermoplastic elastomer composition for slush molding indicated in this gazette, It does not have pliability, rubber elasticity, the low-temperature characteristic, a sex with a crack-proof, and the characteristic satisfying yet enough in respect of abrasion resistance like the slush molding object acquired from the thermoplastic elastomer composition for powder slush molding indicated to above mentioned JP,10-182900,A.

[0006]

[Problem(s) to be Solved by the Invention]The purpose of this invention has good melting mobility, and it excels in the moldability and powder coating nature at the time of performing powder molding, such as slush molding, And it is providing the powdered thermoplastic polymer composition which can manufacture the quality Plastic solid which is excellent in a sex with a crack-proof, and abrasion resistance, and is hard to damage even if it receives friction and contact by high frequency, and is excellent in the upper pliability, rubber elasticity, the low-temperature characteristic, a hand, and appearance, and a coat. The purpose of this invention is to provide the Plastic solid which consists of the aforementioned powdered polymer composition.

[0007]

[Means for Solving the Problem]This invention persons have continued research wholeheartedly that the above-mentioned purpose should be attained. As a result, thermoplastic elastomer which consists of a styrene (hydrogenation) diene system block copolymer is received, (Hydrogenation) A polyurethane system block copolymer which has a styrene diene copolymer block and a thermoplastic polyurethane-polymers block, A thermoplastic polyurethane elastomer and a softener were blended in a specific quantity, a thermoplastic elastomer composition was prepared, the thermoplastic elastomer composition was made into mean particle diameter of 800 micrometers or less, and a powdered thermoplastic polymer composition was manufactured. And when the physical properties were examined about a Plastic solid acquired from a powdered polymer composition obtained by that cause and it, the powdered polymer composition had good melting mobility, and it found out excelling in a moldability at the time of performing powder molding, such as slush molding. A Plastic solid acquired from this powdered polymer composition found out that it is hard to be damaged even if it excels in a sex with a crack-proof, and abrasion resistance and receives friction and contact by high frequency, and excelling also in pliability, rubber elasticity, the low-temperature characteristic, a hand, and appearance moreover, and completed this invention.

[0008]Namely, this invention, (1) From a polymeric block (A1) and a conjugated diene compound which mainly consist of a (i) aromatic vinyl compound, mainly. As opposed to at least one sort of addition condensation system block copolymer (I)100 mass parts chosen from a block copolymer which has a becoming polymeric block (B1), and its hydrogenation thing;

(ii) An addition condensation system block (C) which consists of a block copolymer which has a polymeric block (A2) which mainly consists of an aromatic vinyl compound, and a polymeric block (B-2) which mainly consists of conjugated diene compounds, or its hydrogenation thing, It is 5 - 200 mass part about polyurethane system block copolymer (II) which has a thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D).;

(iii) thermoplastic polyurethane elastomer (III) — 50 to 500 mass part; — and, (iv) It is a powdered polymer composition which consists of a thermoplastic polymer composition which contains softener (IV) at a rate of 10 - 300 mass-part, and is characterized by mean particle diameter being 800 micrometers or less.

[0009]and this invention — (2) powdered polymer composition [of the above (1) whose melt flow rates (MFR) measured under a condition of temperature of 230 ** and 2.16 kg of load according

to JIS K-7210 are 10g/10 minutes or more]; — and, (3) It is above (1) or (2) powdered-polymer-composition; which is an object for slush molding.

[0010]And this invention is a slush molding object which uses one powdered polymer composition of (4) aforementioned (1) - (3).

[0011]

[Embodiment of the Invention]This invention is explained in detail below. Addition condensation system block copolymer (I) used with the powdered polymer composition of this invention, The polymeric block (A1) [it is called the following "aromatic vinyl polymeric block (A1)"] which mainly consists of an aromatic vinyl compound. It consists of at least one sort chosen from the block copolymer which has a polymeric block (B1) [it is called the following "conjugated diene polymer block (B1)"] which mainly consists of conjugated diene compounds, and its hydrogenation thing. Polyurethane system block copolymer (II) used with the powdered polymer composition of this invention, From a conjugated diene compound [polymeric block / which mainly consists of an aromatic vinyl compound / (A2) / [it is called the following "aromatic vinyl polymeric block (A2)"]], mainly. the becoming polymeric block — it is a polyurethane system block copolymer which has the addition condensation system block (C) which consists of a block copolymer which has (B-2 [it is called the following "conjugated diene polymer block (B-2)"]), or its hydrogenation thing, and a thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D).

[0012]The aromatic vinyl polymeric block in addition condensation system block copolymer (I) (A1), And as an aromatic vinyl compound which constitutes the aromatic vinyl polymeric block (A2) in the addition condensation system block (C) of polyurethane system block copolymer (II), For example, styrene, alpha-methylstyrene, beta-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, t-butylstyrene, 2,4-dimethylstyrene, Vinyl aromatic compounds, such as 2,4,6-trimethyl styrene, monofluorostyrene, difluorostyrene, monochlorostyrene, dichlorostyrene, methoxy styrene, and vinylanthracene and vinylanthracene, can be mentioned. Even if an aromatic vinyl polymeric block (A1) and (A2) have a structural unit which consists only of one sort of the above mentioned aromatic vinyl compound, they may have a structural unit which consists of two or more sorts. before long — also coming out — as for an aromatic vinyl polymeric block (A1) and (A2), it is preferred to mainly consist of a structural unit originating in styrene.

[0013]An aromatic vinyl polymeric block (A1) and (A2) may have a little structural units which consist of other copolymeric monomers if needed with the structural unit which consists of an aromatic vinyl compound. As for the rate of the structural unit which consists of other copolymeric monomers in that case, it is preferred that it is below 10 mass % based on an aromatic vinyl polymeric block (A1) or the mass of (A2), and it is more preferred that it is below 5 mass %. As other copolymeric monomers in that case, ionic polymerization nature monomers, such as 1-butene, a pentene, a hexene, butadiene, isoprene, and the methyl vinyl ether, can be mentioned, for example.

[0014]As a conjugated diene compound which constitutes the conjugated diene polymer block (B1) in addition condensation system block copolymer (I), and the conjugated diene polymer block (B-2) in the addition condensation system block (C) of polyurethane system block copolymer (II), butadiene, Isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, etc. can be mentioned. Even if a conjugated diene polymer block (B1) and (B-2) comprise one sort of these conjugated diene compounds, they may comprise two or more sorts. the case where a conjugated diene polymer block (B1) and/or (B-2) have a structural unit originating in two or more sorts of conjugated diene compounds — those connection forms — randomness and a taper — it can consist of block like shape or two or more sorts of those combination in part.

[0015]But before long a conjugated diene polymer block (B1) and (B-2), From a point of the improvement effect of a rubber physical property. An isoprene unit. The polyisoprene block which consists of a monomeric unit made into a subject. Or a part of the unsaturated bond. Or the hydrogenation polyisoprene block to which hydrogenation of all was carried out; hydrogenation polybutadiene block; or the isoprene unit, and butadiene units to which

hydrogenation of a part or all of the polybutadiene block which consists of a monomeric unit which makes butadiene units a subject, or its unsaturated bond was carried out. It is preferred that a part or all of the isoprene / butadiene copolymerization block which consists of a monomeric unit made into a subject, or its unsaturated bond are the hydrogenation isoprene / butadiene copolymerization block by which hydrogenation was carried out.

[0016] In the above-mentioned polyisoprene block which can turn into a conjugated diene polymer block (B1) and/or a configuration block of (B-2). Before the hydrogenation, the unit originating in isoprene, 2-methyl-2-butene-1, 4-diyl group [isoprene unit of $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$; 1 and 4-combination], Isopropenylethylene [$-\text{CH}(\text{C}(\text{CH}_3)=\text{CH}_2)-\text{CH}_2-$; 1 and 4-combination], and the rate in particular of each unit is not limited.

[0017] In the above-mentioned polybutadiene block which can turn into a conjugated diene polymer block (B1) and/or a configuration block of (B-2). Before the hydrogenation, 70-20-mol %, especially 65-40-mol% of the butadiene units are 2-butene-1 and 4-diyl group (butadiene units of $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$; 1 and 4-combination), It is especially preferred that 35-60-mol % is vinyl ethylene [butadiene units of $-\text{CH}(\text{CH}=\text{CH})-\text{CH}_2-$; 1 and 2-combination] 30-80-mol%. When it separates from 70-20-mol the range which is % which 1 in a polybutadiene block and 4-coupling amount described above, the rubber physical property may become poor.

[0018] In above-mentioned isoprene / butadiene copolymerization block which can turn into a conjugated diene polymer block (B1) and/or a configuration block of (B-2). Before the hydrogenation, the unit originating in isoprene 2-methyl-2-butene-1, 4-diyl group, It consists of at least one sort of bases chosen from the group which consists of isopropenylethylene and 1-methyl-1-vinylethylene, The unit originating in butadiene consists of 2-butene-1, a 4-diyl group, and/or vinyl ethylene, and the rate in particular of each unit is not restricted. In isoprene / butadiene copolymerization block, arrangement of an isoprene unit and butadiene units may be which gestalt of the shape of random, block like shape, and the shape of a taper block. And it is preferred that the mole ratios of the point of the improvement effect of a rubber physical property to isoprene unit:butadiene units are 1:9-9:1 in isoprene / butadiene copolymerization block, and it is more preferred that it is 3:7-7:3.

[0019] In addition condensation system block copolymer (I) and polyurethane system block copolymer (II). It is preferred that hydrogenation of a part or all of an unsaturated double bond (double bond between carbon-carbon) in the conjugated diene polymer block (B1) and (B-2) is carried out from the point that heat resistance and weatherability will become good. As for the conjugated diene polymer block in that case (B1), and the hydrogenation rate of (B-2), it is preferred that it is more than 50 mol %, it is more preferred that it is more than 60 mol %, and it is still more preferred that it is more than 80 mol %. The hydrogenation rate of the unsaturated double bond in a conjugated diene polymer block (B1) and (B-2), Before and after hydrogenation, the content of the unsaturated double bond in a conjugated diene polymer block (B1) and (B-2) can be measured according to iodine value measurement, an infrared spectrophotometer (IR), nuclear magnetic resonance (NMR), etc., and can be calculated from the measured value.

[0020] The connection form of the aromatic vinyl polymeric block (A1) and conjugated diene polymer block (B1) in addition condensation system block copolymer (I), And the connection form in particular of the aromatic vinyl polymeric block (A2) and conjugated diene polymer block (B-2) in the addition condensation system block (C) of polyurethane system block copolymer (II) is not restricted, Straight chain shape, branched state, radials, or those two or more may be any of a union ***** connection form, and it is preferred that it is a connection form of straight chain shape.

[0021] The addition condensation system block (C) of addition condensation system block copolymer (I) and/or polyurethane system block copolymer (II), When an aromatic vinyl polymeric block and a conjugated diene polymer block are what has the structure combined with straight chain shape, it is A about an aromatic vinyl polymeric block (A1) and (A2) — a conjugated diene

polymer block (B1) and (B-2) -- B -- a table -- the bottom sometimes, The tetra block structure expressed with the triblock structure expressed with the jib locking structure expressed with A-B, A-B-A, or B-A-B, A-B-A-B, or B-A-B-A or the poly block structure which A and B have combined with five or more piece straight chain shape can be taken. It is preferred from points, such as elasticity, kinetic property, and handling nature, that it is the triblock structure expressed with the jib locking structure or A-B-A expressed with A-B also among them.

[0022]In the thing of the poly block structure more than the above mentioned triblock. Two or more aromatic vinyl polymeric block A may be the blocks of contents which are different even if it is the block of the same contents mutually, and two or more conjugated diene polymer block B may be the blocks of contents which are different even if it is the block of the same contents mutually. For example, two aromatic vinyl polymeric block A in the triblock structure expressed with A-B-A, Or two conjugated diene polymer block B in the triblock structure expressed with B-A-B may have a kind of the aromatic vinyl compound or conjugated diene compound which constitutes them, its coupling case, a the same number average molecular weight of a block, etc., or may differ.

[0023]In the addition condensation system block (C) of addition condensation system block copolymer (I) and polyurethane system block copolymer (II). It is preferred that the content of the structural unit of the viewpoint of the rubber elasticity of the Plastic solid etc. which are acquired from a powdered polymer composition, and pliability to aromatic vinyl compound origin is five to 70 mass %, and it is more preferred that it is five to 40 mass %. The content of the structural unit of the aromatic vinyl compound origin in the addition condensation system block (C) of addition condensation system block copolymer (I) and polyurethane system block copolymer (II) can be calculated with a $^1\text{H-NMR}$ spectrum etc.

[0024]Addition condensation system block copolymer (I) is in the state before hydrogenation, and the number average molecular weight (M_n) 50,000-1,000,000, and that it is especially 50,000-300,000, It is desirable from points, such as the moldability at the time of performing shaping, paint, etc. using a powdered polymer composition, paintwork especially melting mobility, the rubber elasticity of the Plastic solid acquired or a coat, abrasion resistance, and a sex with a crack-proof. The number average molecular weight (M_n) of the addition condensation system block (C) in polyurethane system block copolymer (II), In the state before hydrogenation addition, 20,000-300,000, and that it is especially 50,000-150,000, It is desirable from points, such as the moldability at the time of performing shaping, paint, etc. using a powdered polymer composition, paintwork especially melting mobility, the rubber elasticity of the Plastic solid acquired or a coat, abrasion resistance, and a sex with a crack-proof. With the number average molecular weight (M_n) of the addition condensation system block (C) in addition condensation system block copolymer (I) in this specification, and polyurethane system block copolymer (II). By the gel-permeation-chromatography (GPC) method, the molecular weight of the polystyrene conversion searched for from the standard polystyrene analytical curve is said.

[0025]The addition condensation system block (C) of addition condensation system block copolymer (I) and/or polyurethane system block copolymer (II), Unless the main point of this invention is spoiled, it may have one sort of functional groups, such as a carboxyl group, a hydroxyl group, an acid anhydride group, an amino group, and an epoxy group, or two sorts or more in the inside of a chain, and/or a molecular terminal by the case.

[0026]Polyurethane system block copolymer (II) used with the powdered polymer composition of this invention is the polyurethane system block copolymer which the addition condensation system block (C) and the thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) which have the above-mentioned block structure combined. Although in particular the hardness and melt viscosity of polyurethane system block copolymer (II) are not limited, generally the hardness (JIS A hardness) by JIS K 6301 (the A method) is 60-95, It is preferred that the melt viscosity at 200 ** is 500-2,000Paands from points, such as powder molding, the moldability at the time of carrying out powder coating, paintwork, the pliability of the Plastic solid acquired or a coat, abrasion resistance, a sex with a crack-proof,

and kinetic property.

[0027]As long as the thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) in polyurethane system block copolymer (II) is a block which consists of thermoplastic polyurethane elastomers, any may be sufficient as it. But before long a thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D), Being formed from thermoplastic polyurethane elastomer (III) mentioned later, congener, or the approximated thermoplastic polyurethane elastomer, It is desirable from the point that the compatibility of the polymers in a powdered polymer composition becomes good, and the kinetic property of the Plastic solid moreover acquired from a powdered polymer composition or a coat becomes good.

[0028]The thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) in polyurethane system block copolymer (II), It is preferred that the point that the rubber physical property of a powdered polymer composition will become better to the number average molecular weight (M_n) is 10,000–500,000, and it is more preferred that it is 30,000–300,000. Here, the number average molecular weight (M_n) of the thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) in this specification means the molecular weight of the polystyrene conversion measured by the gel-permeation-chromatography (GPC) method.

[0029]Polyurethane system block copolymer (II), the jib which has one addition condensation system block (C) and one thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D), even if it is a lock copolymer, Or an addition condensation system block (C) and a thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) may be three pieces or the poly block copolymer united four or more pieces in total. From points, such as the compatibility of the polymers in a powdered polymer composition, dynamics physical properties, and a moldability. the jib which one addition condensation system block (C) and one thermoplastic polyurethane ERASUTO multiple independently targetable reentry vehicle lock (D) combined — a lock copolymer. and/or — it is preferred that it is the triblock copolymer which one (D) combined with two (C) — a jib — it is more preferred that it is a lock copolymer.

[0030]What the manufacturing method in particular of addition condensation system block copolymer (I) and polyurethane system block copolymer (II) is not restricted, but may manufacture it by which method as long as it is a method that each above-mentioned block copolymer can be manufactured, and is already marketed may be used.

[0031]Although not limited at all, addition condensation system block copolymer (I) can be manufactured by ionic polymerization methods, such as anionic polymerization and cationic polymerization, the single site polymerizing method, a radical polymerization method, etc., for example. When based on an anionic polymerization method, for example, using an alkyl lithium compound etc. as a polymerization initiator in inert organic solvents, such as n-hexane and cyclohexane, It can manufacture by carrying out successive polymerization of an aromatic vinyl compound and the conjugated diene compound, adding active hydrogen compounds, such as alcohols, carboxylic acid, and water, and stopping a polymerization, after manufacturing the block copolymer which has desired molecular structure and molecular weight. And the block copolymer manufactured with the above can be hydrogenated under existence of a hydrogenation catalyst in an inert organic solvent in accordance with a desirable publicly known method, and addition condensation system block copolymer (I) by which hydrogenation was carried out can be obtained.

[0032]Although not limited at all, polyurethane system block copolymer (II), Have a thermoplastic polyurethane elastomer, and an aromatic vinyl polymeric block (A2) and a conjugated diene polymer block (B-2), and at the end For example, a functional group, The addition condensation system block copolymer which has a hydroxyl group preferably, and/or its hydrogenation thing (it may be called the following "terminal modification addition condensation system block copolymer") are made to knead and react under a melting condition, It can obtain from the polyurethane system resultant acquired by that cause by extracting and collecting polyurethane system block copolymer (II)s. In that case, the melt kneading of a thermoplastic polyurethane

elastomer and a terminal modification addition condensation system block copolymer can perform [use] melt kneading devices, such as a single screw extruder, a biaxial extrusion machine, a kneader, and a Banbury mixer. Although melt kneading conditions can be chosen according to the kind of the thermoplastic polyurethane elastomer to be used or terminal modification addition condensation system block copolymer, the kind of device, etc., they are good for a for [1 to 15 minutes] grade to carry out at the temperature of 180–250 ** generally.

[0033]Polyurethane system block copolymer (II) can be manufactured also by methods other than the above-mentioned method. For example, in the middle of the beginning of the reaction at the time of making polymers diol, organic diisocyanate, and a chain extension agent react in an extrusion machine etc., and manufacturing a thermoplastic polyurethane elastomer, or a reaction. The polyurethane system resultant which contains polyurethane system block copolymer (II) by adding a terminal modification addition condensation system block copolymer to the system of reaction is made to form. It can obtain also by extracting and collecting polyurethane system block copolymer (II)s from the polyurethane system resultant.

[0034]In the above, extraction and recovery of polyurethane system block copolymer (II) from a polyurethane system resultant. For example, a polyurethane system resultant is pulverized in a suitable size if needed. Process it with the good solvent of polyurethane, such as dimethylformamide, and an unreacted thermoplastic polyurethane elastomer is extracted and removed. Subsequently, it can carry out by processing with the good solvent of terminal modification addition condensation system block copolymers, such as cyclohexane, carrying out extraction removal of the unreacted terminal modification addition condensation system block copolymer, and drying the remaining solid.

[0035]In the above-mentioned terminal modification addition condensation system block copolymer used for manufacture of polyurethane system block copolymer (II). It originates in the manufacturing method mentioned later, and the addition condensation system block copolymer which does not have a functional group at the end, and/or its hydrogenation thing, i.e., the polymer equivalent to addition condensation system block copolymer (I), are contained in many cases. Therefore, the polyurethane system resultant acquired by the reaction of a thermoplastic polyurethane elastomer and a terminal modification addition condensation system block copolymer, It is a mixture of polyurethane system block copolymer (II), an unreacted thermoplastic polyurethane elastomer, addition condensation system block copolymer (I), and four persons of a terminal modification addition condensation system block copolymer in many cases. From this, in manufacture of the powdered polymer composition of this invention, With addition condensation system block copolymer (I), polyurethane system block copolymer (II), thermoplastic polyurethane elastomer (III), and softener (IV). Blend a terminal modification addition condensation system block copolymer, and the polyurethane system resultant which a terminal modification addition condensation system block copolymer and thermoplastic polyurethane elastomer (III) were made to react, and was described above in the constituent is made to form. The method [namely, method of making it exist in a constituent with the gestalt of a resultant, without collecting polyurethane system block copolymer (II)s from a polyurethane system resultant] of making the polyurethane system resultant existing as it is in a constituent may be used.

[0036]Here, the terminal modification addition condensation system block copolymer used for manufacture of polyurethane system block copolymer (II) can be manufactured by the following anionic polymerization methods, for example. Namely, use an alkyl lithium compound etc. as an initiator and in inert organic solvents, such as n-hexane and cyclohexane. When successive polymerization of an aromatic vinyl compound and the conjugated diene compound is carried out and desired molecular structure and molecular weight are reached, The compound which has oxirane skeletons, such as ethyleneoxide, propylene oxide, and styrene oxide. Or it can manufacture by making lactone system compounds, such as epsilon-caprolactone, beta propiolactone, and dimethyl propiolactone (PIBARO lactone), etc. add, adding active hydrogen containing compounds, such as alcohols, carboxylic acid, and water, subsequently, and suspending a polymerization. And the block copolymer obtained by that cause preferably, In inert

organic solvents, such as n-hexane and cyclohexane, an alkylaluminum compound and a cobalt compound, The terminal modification addition condensation system block copolymer by which hydrogenation was carried out can be obtained by hydrogenating under existence of hydrogenation catalysts, such as a Ziegler catalyst which consists of nickel compounds etc., under the reaction temperature of 20–150 **, hydrogen pressure 0.1 – the conditions of 15MPa.

[0037]When it is what has straight-chain-shape structure, the terminal modification addition condensation system block copolymer may have one hydroxyl group in one end of a molecule, or may have two hydroxyl groups to the both ends of a molecule. When a terminal modification addition condensation system block copolymer is what has a branched state or radiate structure, it may have one piece or a hydroxyl group [two or more (the number of branching)] in the molecular terminal. As for the number of the terminal hydroxyl groups per molecule of a terminal modification addition condensation system block copolymer, it is preferred that it is 0.5–1 piece, and it is more preferred that it is 0.7–1 piece.

[0038]Generally thermoplastic polyurethane elastomer (III) used with the powdered polymer composition of this invention is manufactured by the reaction of polymers diol, organic diisocyanate, and a chain extension agent. The polymers diol used for manufacture of thermoplastic polyurethane elastomer (III), Kinetic property acquired from the powdered polymer composition of this invention in which it contains thermoplastic polyurethane elastomer (III) that the number average molecular weight is 1,000–6,000, such as a Plastic solid and a coat, It is desirable from the point that abrasion resistance, a sex with a crack-proof, heat resistance, the low-temperature characteristic, elastic recovery nature, etc. become good. Here, the number average molecular weight of polymers diol as used in this specification is a number average molecular weight computed based on the hydroxyl value measured based on JIS K1557.

[0039]As an example of the polymers diol which can be used for manufacture of thermoplastic polyurethane elastomer (III), Polyesterdiol, polyetherdiol, polyester etherdiol, Polycarbonatediol, polyester polycarbonate diol, etc. can be mentioned and thermoplastic polyurethane elastomer (III) can be formed using one sort of these polymers diol, or two sorts or more.

[0040]As the above-mentioned polyesterdiol which can be used for manufacture of thermoplastic polyurethane elastomer (III), The polyesterdiol obtained by the reaction of at least one sort of dicarboxylic acid components and low molecule diol which are chosen from aliphatic dicarboxylic acid, aromatic dicarboxylic acid, and those ester plasticity derivatives, The polyesterdiol etc. which are obtained by the ring opening polymerization of lactone can be mentioned. More specifically as said polyesterdiol, For example, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, Sebacic acid, dodecanedioic acid, etc. preferably One sort or two sorts or more, aromatic dicarboxylic acid, such as aliphatic dicarboxylic acid of the carbon numbers 6–12, terephthalic acid, isophthalic acid, and alt.phthalic acid, and those ester plasticity derivatives, For example, ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, The polyesterdiol produced by making carry out the polycondensation reaction of one sort of aliphatic series diol of the carbon numbers 2–10, or the two sorts or more preferably, such as 3-methyl-1,5-pentanediol and 2-methyl-1,8-octanediol, Polycaprolactone diol and polyvalerolactonediol can be mentioned.

[0041]As the above-mentioned polyetherdiol which can be used for manufacture of thermoplastic polyurethane elastomer (III), a polyethylene glycol, a polypropylene glycol, polytetramethylene glycol, etc. can be mentioned, for example. As the above-mentioned polycarbonatediol which can be used for manufacture of thermoplastic polyurethane elastomer (III), For example, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, One sort or two sorts or more of aliphatic series diol, such as 1,8-octanediol, 1,9-nonanediol, and 2-methyl-1,8-octanediol, The polycarbonatediol produced by making carbonic ester or phosgene, such as diphenyl carbonate and dialkyl carbonate, react can be mentioned.

[0042]Although the kind in particular of organic diisocyanate used for manufacture of thermoplastic polyurethane elastomer (III) is not limited, one sort of with a molecular weight of 500 or less aromatic diisocyanate, cycloaliphatic diisocyanate, and aliphatic series diisocyanate or two sorts or more are used preferably. As an example of such organic diisocyanate, 4 and 4'-diphenylmethane diisocyanate, toluene diisocyanate, p-phenylene diisocyanate, xylylene

diisocyanate, naphthalene diisocyanate, The hydrogenation 4, 4'-diphenylmethane diisocyanate (4 and 4'-dicyclohexylmethane diisocyanate), Isophorone diisocyanate, hexamethylene diisocyanate, etc. can be mentioned and 4 and 4'-diphenylmethane diisocyanate is preferably used also among these organic diisocyanate.

[0043]any of the chain extension agent used for manufacture of a thermoplastic polyurethane elastomer from the former as a chain extension agent which can be used for manufacture of thermoplastic polyurethane elastomer (III) — although — it can be used and the kind in particular is not limited. But one sort in aliphatic series diol, alicyclic diol, and aromatic diol or two sorts or more are preferably used as a chain extension agent before long. As an example of the chain extension agent used preferably, Ethylene glycol, a diethylene glycol, 1,4-butanediol, Diol, such as 1,5-pentanediol, 2-methyl-1,3-propanediol, 1,6-hexanediol, neopentyl glycol, 1,9-nonanediol, cyclohexanediol, and 1,4-bis(beta-hydroxyethoxy)benzene, can be mentioned. Also while describing above, aliphatic series diol of the carbon numbers 2-6 is used more preferably as a chain extension agent, and 1,4-butanediol is used still more preferably.

[0044]In the powdered polymer composition of this invention, as thermoplastic polyurethane elastomer (III), Polymers diol, a chain extension agent, and organic diisocyanate, Polymers diol : so that it may be the range of chain extension agent = 1:0.2 - 8.0 (mole ratio) and may be the range of [number of sum total mols of polymers diol and chain extension agent]:[number of mols of organic diisocyanate] = 1:0.98 - 1.04. The thermoplastic polyurethane elastomer which carries out, and is produced by making react is used preferably. The powdered polymer composition of this invention containing such thermoplastic polyurethane elastomer (III) does not have the rapid rise of melt viscosity at the time of shaping and paint, etc., and a Plastic solid, a coat, etc. which are made into the purpose can be manufactured smoothly. And heat resistance, such as a Plastic solid acquired by that cause and a coat, abrasion resistance, and a sex with a crack-proof will become good.

[0045]Thermoplastic polyurethane elastomer (III) used with the powdered polymer composition of this invention is preferred from kinetic property, such as a Plastic solid in which it is acquired from a powdered polymer composition that the above-mentioned JIS-A hardness is 60-95, and a coat, becoming good, and having moderate hardness. If the kinetic property of the Plastic solid acquired from a powdered polymer composition as the JIS-A hardness of thermoplastic polyurethane elastomer (III) is less than 60, or a coat becomes low easily and exceeds 95 on the other hand, the pliability of a Plastic solid or a coat will fall easily. As for the number average molecular weight (M_n) of thermoplastic polyurethane elastomer (III), it is preferred from points, such as melting mobility in the time of powder molding and powder coating, etc., that it is 150,000 or less. The number average molecular weight (M_n) of polyurethane elastomer (III) here is a molecular weight of the polystyrene conversion searched for by gel-permeation-chromatography (GPC) measurement.

[0046]The manufacturing method in particular of thermoplastic polyurethane elastomer (III) may not be limited, but may use above-mentioned polymers diol, organic diisocyanate, and chain extension agent, and may manufacture them by any of the prepolymer method and a one-shot process using a publicly known urethane-ized reaction. It is preferred to carry out melt polymerization under the absence of a solvent substantially but [before long], and it is preferred to manufacture by continuation melt polymerization using a multiaxial screw die pressing appearance machine especially.

[0047]As an example which can use a publicly known thing as softener (IV) in the powdered polymer composition of this invention, Hydrocarbon system oils, such as paraffin series, a naphthene system, an aromatic system, and a liquid paraffin; Peanut oil, vegetable oil [, such as rosin,]; -- phosphoric ester; -- low molecular weight polymer, such as a chlorinated paraffin, low molecular weight polyethylene, and a polyethylene glycol, etc. can be mentioned, and these one sort or two sorts or more can be used. But a paraffin hydrocarbon system oil is used preferably before long.

[0048]The powdered polymer composition of this invention receives addition condensation system block copolymer (I) 100 mass part, It is required to contain five to 200 mass part and thermoplastic polyurethane elastomer (III) by 50 to 500 mass part, and to contain softener (IV)

for polyurethane system block copolymer (II) at a rate of ten to 300 mass part. The loadings of polyurethane system block copolymer (II) receive addition condensation system block copolymer (I) 100 mass part, The melting mobility of a powdered polymer composition falls that they are less than five mass parts, it comes to be inferior to a moldability, paintwork, etc., and kinetic property, such as abrasion resistance, such as a Plastic solid moreover acquired and a coat, a sex with a crack-proof, and breaking strength, declines. On the other hand, if the loadings of polyurethane system block copolymer (II) exceed 200 mass parts to addition condensation system block copolymer (I) 100 mass part, kinetic property, such as abrasion resistance, a sex with a crack-proof, and breaking strength, will decline. The loadings of thermoplastic polyurethane elastomer (III) receive addition condensation system block copolymer (I) 100 mass part, If kinetic property, such as abrasion resistance, a sex with a crack-proof, and breaking strength, declines that they are less than 50 mass parts and 500 mass parts are exceeded on the other hand, kinetic property, such as pliability, such as a Plastic solid acquired from a powdered polymer composition and a coat, abrasion resistance, a sex with a crack-proof, and breaking strength, will decline. The loadings of softener (IV) receive addition condensation system block copolymer (I) 100 mass part, If the melting mobility of a powdered polymer composition falls that they are less than ten mass parts, a moldability becomes poor, and pliability and the low-temperature characteristic fall and 300 mass parts are exceeded on the other hand, Kinetic property, such as abrasion resistance, such as a Plastic solid acquired from a powdered polymer composition and a coat, a sex with a crack-proof, and breaking strength, etc. decline.

[0049] As for the powdered polymer composition of this invention, it is preferred to contain polyurethane system block copolymer (II) at a rate of 50-150 to addition condensation system block copolymer (I) 100 mass part. It is preferred to contain thermoplastic polyurethane elastomer (III) at a rate of 200 to 400 mass part to addition condensation system block copolymer (I) 100 mass part. It is preferred to contain softener (IV) at a rate of 50 to 200 mass part to addition condensation system block copolymer (I) 100 mass part.

[0050] The powdered polymer composition of this invention may contain lubricant further if needed. If lubricant is contained, the frictional resistance of the surface of the Plastic solid acquired from the powdered polymer composition of this invention or a coat will decrease, and a sex with a crack-proof and abrasion resistance will improve as the result. As lubricant, can use a publicly known thing and For example, fatty-acid-amide; silicone oil, such as oleic amide, silicone series compound [, such as impalpable powder of silicone / acrylic polymerization,]; -- fluorine compound [, such as fluorinated hydrocarbon oil and polytetrafluoroethylene,]; -- polyethylene oxide. Polyalkylene oxide, such as polypropylene oxide; impalpable powder, such as ester oil and ultra high molecular weight polyethylene, etc. can be mentioned, and these one sort or two sorts or more can be used.

[0051] The powdered polymer composition of this invention may contain the reinforcing agent for rubbers if needed. Content of the reinforcing agent for rubbers will raise the kinetic property of the Plastic solid etc. which are acquired, abrasion resistance, and a sex with a crack-proof. A publicly known thing can be used as a reinforcing agent for rubbers. For example, carbon black; carbon fiber; poval system ** fibrillation textiles, such as HAF, HAF-HS, SAF, and ISAF; organic fibrous material, such as a nylon fiber and polyester fiber, etc. can be mentioned, and these one sort or two sorts or more can be contained. It is preferably used from the Plastic solid which excels [fibrous material / carbon black, carbon fiber, and/or / organic] in pliability and lightweight nature being acquired but before long.

[0052] If the powdered polymer composition of this invention is a range which does not spoil the main point of this invention, If needed Other thermoplastics, for example, various polyethylene, various polypropylene, Polyolefin system resin, such as an ethylene-propylene random copolymer and an ethylene-vinylacetate copolymer; one sort, such as styrene resin, such as polystyrene, poly alpha-methylstyrene, and a styrene acrylonitrile copolymer, or two sorts or more may be contained. The powdered polymer composition of this invention may contain a thermostabilizer, an antioxidant, light stabilizer, fire retardant, a spray for preventing static electricity, etc. if needed. The powdered polymer composition of this invention may contain organic fillers, such as inorganic fillers, such as the softening agent which does not show a reinforcing effect, for

example, calcium carbonate, talc, silica, and diatomaceous earth, a rubber crumb, wood flour, etc.

[0053]The powdered polymer composition of this invention requires that the mean particle diameter should be 800 micrometers or less, and it is preferred that it is 500 micrometers or less. If the mean particle diameter of a powdered polymer composition exceeds 800 micrometers, the particulate flow kinesis and measuring nature in the time of powder molding or powder coating, etc. will become poor. Especially when using the powdered polymer composition of this invention for slush molding, it is preferred that the mean particle diameter is 450 micrometers or less from points, such as the homogeneity of the thickness of the Plastic solid acquired, occurrence prevention of a pinhole, and dynamics intensity. Here, the mean particle diameter of the powdered polymer composition in this specification means the mean particle diameter measured with the scatter type particle size distribution measuring device (for example, product made from HORIBA "LA-920").

[0054]The powdered polymer composition of this invention mixes [package-] or mixes [division-] each above-mentioned ingredient which constitutes a constituent. The mixture obtained by that cause A conventionally publicly known kneading machine, for example, a 1 axis extrusion machine, A twin screw extruder, a Banbury mixer, Brabender, an open roll, It can obtain by kneading using kneading machines, such as a kneader, for example, preparing a pellet form-like thermoplastic polymer composition, carrying out disintegration of the thermoplastic polymer composition obtained by that cause by a suitable method, and classifying using a screen etc. as occasion demands. Said kneading for obtaining a thermoplastic polymer composition is faced, If a kneading machine is supplied after using mixers, such as a Henschel mixer and a tumbler, and carrying out a dry blend beforehand before kneading, without supplying each of an ingredient to be kneaded to a kneading machine directly as it is, a uniform thermoplastic polymer composition can be obtained. Generally as a kneading temperature for preparing a thermoplastic polymer composition, the temperature of 150-250 ** is adopted preferably.

[0055]Any may be sufficient as long as it is a method which the method in particular of disintegration is not restricted but can carry out pulverization of the thermoplastic polymer composition, The pellet of a thermoplastic polymer composition, etc. For example, a turbo mill, a pin mill, How to pulverize under ordinary temperature or freezing using shock type fine grinding devices, such as a hammermill and a rotor speed mill, Heat melting of the thermoplastic polymer composition is carried out, and when obtaining the method and thermoplastic polymer composition which are sprayed and cooled using a spray device, a disk atomiser, etc. with an extrusion machine, it can manufacture by the method of carrying out a hot cut underwater through a micro dice, etc. Before long, but, the method of crushing equipment of pulverizing under ordinary temperature or freezing using a shock type fine grinding device is cheap, and production is preferably adopted from an easy point.

[0056]By the above-mentioned disintegration method, mean particle diameter may use the powder as a powdered polymer composition of this invention as it is, when powder of 800 micrometers or less is obtained directly. The case where the mean particle diameter of the powdered polymer composition obtained by disintegration exceeds 800 micrometers, when [even if it is 800 micrometers or less,] you want to obtain the powdered polymer composition whose mean particle diameter is still smaller, and when, It is good to classify the powder obtained by the above-mentioned disintegration method using a screen, a dust collection device, etc., and to collect and use the powder whose mean particle diameter is smaller than 800 micrometers or less or it.

[0057]As for the powdered polymer composition of this invention, it is preferred that the melt flow rates (MFR) measured under the condition of the temperature of 230 ** and 2.16 kg of load according to JIS K-7210 are 10g/10 minutes or more, and it is more preferred that they are 30g/10 minutes or more. When said MFRs of a powdered polymer composition are 10g/less than 10 minutes, at the time of slush molding or other powder molding, melt viscosity becomes high at the time of powder coating, a moldability and mobility fall, it becomes easy to produce a pinhole and thickness spots in a Plastic solid or a coat, and weld strength may fall.

[0058]In the Plastic solid acquired from the powdered polymer composition of this invention, and

it. It is preferred to have the phase structure of the sea-island type which the phase which thermoplastic polyurethane elastomer (III) forms a matrix phase (continuous phase) substantially, and consists of addition condensation system block copolymer (I) and softener (IV) into this matrix distributed in the state of detailed particles substantially. When it has the phase structure of such a sea-island type, an advanced sex with a crack-proof and abrasion resistance are effectively demonstrated from thermoplastic polyurethane elastomer (III) by the matrix phase which becomes substantial. With and the detailed particulate material phase which consists of addition condensation system block copolymer (I) having the outstanding pliability and rubber elasticity, and softener (IV). thermoplastic polyurethane elastomer (III) -- compared with the case of being independent, the pliability and rubber elasticity in the Plastic solid etc. which are acquired from a powdered polymer composition are markedly alike, and improve.

[0059] In the Plastic solid acquired from the powdered polymer composition of this invention, and it, it can check having the phase structure of the above-mentioned sea-island type by observation by a scanning electron microscope, for example. For example, a 1-mm-thick sheet like object is built by slush molding using a powdered polymer composition, and after immersing it into liquid nitrogen and fully cooling, it fractures promptly. Ion sputtering is performed, after etching the fracture surface, without doing physical damage by immersing the fractured sample for 1 minute at a room temperature into cyclohexane, carrying out dissolution removal of addition condensation system block copolymer (I) and softener (IV) and drying it. If the fracture surface processed such is observed with a scanning electron microscope, signs that it is distributing without connecting the holes (hollow) which adjoined each other will be checked. By it, the phase which consists of thermoplastic polyurethane elastomer (III) forms a matrix phase (continuous phase) substantially, It can check making the phase structure of the sea-island type which the particles which become substantial are distributing with island shape from addition condensation system block copolymer (I) and softener (IV) in this matrix phase.

[0060] In the Plastic solid acquired from the powdered polymer composition of this invention, and it, Although the particle diameter in particular of the particulate material which becomes substantial is not restricted from addition condensation system block copolymer (I) and softener (IV), When the phase structure is investigated at the process of the above-mentioned series of consisting of scanning electron microscope observation of the etching ion sputtering fracture surface by cooling-fracture-cyclohexane by the manufacture-liquid nitrogen of a sheet like object with a thickness [by the above-mentioned method, i.e., slush molding,] of 1 mm, It is preferred that it is the particle diameter that the average value (L_s) of the major axis of about 1000 holes formed by etching is set to 5 micrometers or less, and it is more preferred that it is the particle diameter which is set to 3 micrometers or less. The average value (L_s) of a major axis is calculated from formula: $L_s = (\sum L) / n$ [L shows the major axis (micrometer) of each hole among a formula, and n shows the number of a hole].

[0061] The powdered polymer composition of this invention can be used effective in the forming technique using a thermoplastic powdered polymer, or paint art. For example, slush molding, compression molding, powder thermal spraying, rotational casting, extrusion molding, It can use for the various paint art (for example, a fluidized bed coating process, electrostatic spray painting, a spraying process, spraying, etc.) using powder molding, such as calender molding, and a granular material, and the various Plastic solids and coat (coated product) of a sheet like object, a film state thing, a hollow shape thing, laminated material, etc. can be obtained by it. But especially the powdered polymer composition of this invention fits the use to slush molding before long. By performing powder molding, such as slush molding, using the powdered polymer composition of this invention, the Plastic solid of the shape of epidermis which has irregular patterns and complicated shape, such as the shape of a leather crimp and a letter of a stitch, can be acquired, for example. And the Plastic solid and coat which are obtained using the powdered polymer composition of this invention are extremely excellent in a sex with a crack-proof, and abrasion resistance, and, moreover, excellent also in pliability, rubber elasticity, the low-temperature characteristic, dynamic strength, etc. Surface coating of the Plastic solid and coat which are obtained using the powdered polymer composition of this invention may be carried out with polyurethane, high slidability polyethylene, etc. if needed.

[0062] A Plastic solid, a coat, etc. of this invention which use a powdered polymer composition. Various characteristics, such as the outstanding characteristic especially advanced abrasion resistance, a sex with a crack-proof, pliability, rubber elasticity, the low-temperature characteristic, and dynamic strength, are harnessed. For example, an instrument panel, a door trim, a console box, Automotive interior material; sofas, such as an armrest, a headrest, a seat, a pillar, a steering wheel, and a ceiling, the skin material; sporting-goods; leisure-goods; stationery; toy for various chairs; it can be used effective in broad uses, such as a lining material of a house.

[0063]

[Example] Although an example etc. explain this invention concretely below, this invention is not limited at all by the following examples. In the following examples, the mean particle diameter of a powdered polymer composition, a moldability (MFR), Measurement or evaluation of slush molding nature, a dispersed particle diameter (morphology) and the sex with a crack-proof of the Plastic solid acquired from the powdered polymer composition, abrasion resistance, rubber elasticity (permanent set), pliability (hardness), and tensile strength was performed by the following methods.

[0064] (1) Mean particle diameter of a powdered polymer composition : mean particle diameter was measured using the powdered polymer composition obtained in the following examples with a dispersion type particle-size-analysis device (product made from HORIBA "LA-920").

[0065] (2) The moldability (MFR) of a powdered polymer composition : using the powdered polymer composition obtained in the following examples, according to JIS K-7210, MFR (melt flow rate) in 230 ** and 2.16 kg loads was measured, and it was considered as the index of the moldability.

[0066] (3) Slush molding nature : the appearance and the surface state of the 1-mm-thick sheet which carried out slush molding using the powdered polymer composition obtained in the following examples were observed by viewing, and slush molding nature was evaluated in accordance with the following valuation basis.

[The valuation basis of slush molding nature]

O : the sheet in which a surface state is very smooth is obtained.

O : a surface state is good and the sheet without a pinhole is obtained.

** : Some rough deposit is shown in the surface and a pinhole is observed in part.

x : Surface unevenness is intense and many pinholes are seen.

[0067] The dispersed particle diameter in a powdered polymer composition (Plastic solid) (morphology) : (4) After cooling a slush molding sheet with a thickness of 1 mm obtained in the following examples with liquid nitrogen, Make it fracture, etch the fracture surface for 1 minute with cyclohexane, dry, and after carrying out ion sputtering, by observing with a scanning electron microscope ("JSM-T100" by JEOL datum incorporated company). The state where the phase which consists of addition condensation system block copolymer (I) and softener (IV) into the matrix phase which consists of thermoplastic polyurethane elastomer (III) is distributing with particle state is checked. Furthermore, dissolution removal of addition condensation system block copolymer (I) and softener (IV) was carried out by etching, the major axis was measured about about 1000 holes formed by dissolution removal of addition condensation system block copolymer (I) and softener (IV), the average value was taken, and it was considered as the dispersed particle diameter.

[0068] The sex with a crack-proof of a Plastic solid (both-way sliding examination by cotton) : (5) Pile up two sheets with a thickness of 1 mm which carried out slush molding using the powdered polymer composition obtained in the following examples, carry out thermal melting arrival, and a 2-mm-thick sheet is produced. From this sheet to length x width x thickness = the specimen of 50 mm x 150 mm x 2-mm size is cut off, and both-way sliding of this specimen top is carried out for 10 minutes covering a length of 140 mm by the surface of cloth made from cotton which added load (one round trip in 1 second comparatively). Load was changed, this examination was done, load when the crack stuck was measured, and it was considered as the index of the sex with a crack-proof. It gets damaged, and the sex with a crack-proof is excellent, so that the value of load is high.

[0069]Abrasion resistance of a Plastic solid (abrasion loss) : (6) Pile up two sheets with a thickness of 1 mm which carried out slush molding using the powdered polymer composition obtained in the following examples, carry out thermal melting arrival, and a 2-mm-thick sheet is produced, A disc-like specimen 110 mm in diameter was pierced from this sheet, abrasion loss was measured according to JIS K-6264 using this specimen, and it was considered as the wear-resistant index. In doing this examination, the thing equivalent to H22 said to JIS was used as a wear ring. It excels in abrasion resistance, so that there is little abrasion loss.

[0070]Rubber elasticity of a Plastic solid (permanent set) : (7) Pile up two sheets with a thickness of 1 mm which carried out slush molding using the powdered polymer composition obtained in the following examples, carry out thermal melting arrival, and a 2-mm-thick sheet is produced, The dumbbell-like No. 1 specimen was pierced from this sheet, the permanent set after 100% extension was measured according to JIS K-6262, and it was considered as the index of rubber elasticity. It excels in rubber elasticity, so that a permanent set is low.

[0071]Pliability of a Plastic solid (hardness) : (8) Pile up two sheets with a thickness of 1 mm which carried out slush molding using the powdered polymer composition obtained in the following examples, carry out thermal melting arrival, and a 2-mm-thick sheet is produced, The length x width x thickness = 110mmx110mmx2mm sheet-shaped specimen was cut out from this sheet, hardness was measured with the type A durometer according to JIS K-6253 using this specimen, and it was considered as the index of pliability.

[0072]Tensile strength of a Plastic solid : (9) Pile up two sheets with a thickness of 1 mm which carried out slush molding using the powdered polymer composition obtained in the following examples, carry out thermal melting arrival, and a 2-mm-thick sheet is produced, The dumbbell-like No. 5 specimen was pierced from this sheet, the tensile test was done according to JIS K-6251 using this specimen, the intensity at the time of a fracture was measured, and it was considered as tensile strength.

[0073]The contents and the cable address of each ingredient which were used in the following examples are as follows.

(i-1) addition condensation system block copolymer (I-1) (cable address: SEPS): -- the hydrogenation thing (number average molecular weight = 100,000 and styrene content = 30 mass %) of the triblock copolymer which consists of a polystyrene block polyisoprene block polystyrene block The hydrogenation rate in a polyisoprene block = 98%.

(i-2) An addition condensation system block copolymer. (I-2) : Hydrogenation thing [number average molecular weight = 150,000 of the triblock copolymer which consists of a polystyrene block poly (isoprene/butadiene) block polystyrene block, styrene content = 30 mass % (cable address: SEEPS), The hydrogenation rate in a poly (isoprene/butadiene) block = 98%].

[0074](ii) A polyurethane system block copolymer. (II). (Cable address-U/SEPS) the hydrogenation thing (SEPS-OH) (number average molecular weight = 80,000 and styrene content = 30 mass %) of the triblock copolymer which consists of a :polystyrene block polyisoprene block polystyrene block, and has a hydroxyl group in one end of a molecule The hydrogenation rate in a polyisoprene block = 98% and number of average hydroxyl groups = 0.9 piece /, and molecule 100 mass part, The dry blend of the thermoplastic polyurethane (TPU1180) 100 following mass part is carried out, Using a twin screw extruder (made in a plastic engineering research institute "BT-30"), 220 ** of cylinder temperatures, Extrusion after carrying out melt kneading under conditions with a screw speed of 150 rpm, Cut, build a pellet and extraction removal of the unreacted polyurethane is carried out using dimethylformamide from the pellet obtained by that cause, subsequently, the jib which the thermoplastic polyurethane (TPU1180) obtained by carrying out extraction removal of unreacted SEPS-OH using cyclohexane, and drying the solid which remained, and an addition condensation system block copolymer (SEPS) combined -- a lock copolymer.

[0075](iii) Thermoplastic polyurethane (III) (cable address: TPU1180) : polyester system thermoplasticity polyurethane elastomer ("Kula Miron U 1180" By Kuraray; polyester system polyurethane elastomer which uses aliphatic polyester as a soft segment).

[0076](iv) Softener (IV) (cable address :P W-380.) : paraffin series process oil ("Diana process PW-380" by Idemitsu petrochemical incorporated company).

[0077]<<Examples 1-4 and the comparative examples 1-3>>

(1) According to the combination shown in the following Table 1 (examples 1-4) and 2 (comparative examples 1-3), After having carried out package mixing of each ingredient using the mixer, supplying the mixture obtained by that cause to the twin screw extruder ("TEM-35B" by Toshiba Machine Co., Ltd.) and kneading for about 5 minutes at 230 **, it extruded and cut to strand shape and the thermoplastic polymer composition of the pellet type was prepared.

(2) The thermoplastic polymer composition of the pellet type obtained above (1), After grinding at temperature-100 ** using an impact type pulverizer (made in Fritsch "rotor speed mill P-14"), screen analysis of the grinding thing was carried out using 32 mesh sieves (0.495 mm of openings), the powder which passed the screen was collected, and it was considered as the powdered polymer composition. When the mean particle diameter of the powdered polymer composition obtained by this was measured by the aforementioned method, it was as being shown in the following Table 1 and 2. When investigated by the method which described above the moldability (MFR) of the obtained powdered polymer composition, it was as being shown in the following Table 1 and 2.

[0078](3) The powdered polymer composition obtained above (2) is uniformly sprinkled over the mold which consists of a nickel electrocasting board (vertical x horizontal x thickness =150mmx150mmx1mm) with a skin temperature of 280 **, After holding to the temperature for 30 seconds and making it weld a powdered polymer composition in the state of settlement, the end of non-welding powder is made to discharge, into a 280 ** heating furnace, it was held for 1 minute and melting was carried out. Subsequently, it took out from the heating furnace, and unmolded after water-cooling at 40 **, and the 1-mm-thick sheet-shaped slush molding object was manufactured. When the method which described above the slush molding nature at this time estimated, it was as being shown in the following Table 1 and 2. When the dispersed particle diameter in a powdered polymer composition (Plastic solid) was measured by the above-mentioned method using the sheet-shaped slush molding object with a thickness [this] of 1 mm, it was as being shown in the following Table 1 and 2.

[0079](4) A 1-mm-thick sheet-shaped slush molding object is manufactured by the same method as the method of the above (3), It was made to pile up each other's two sheet-shaped slush molding objects acquired by that cause, and again, it held for 3 minutes in a 280 ** heating furnace, thermal melting arrival was performed, it took out from the heating furnace, and the 2-mm-thick sheet-shaped slush molding object which is unmolded and is used for the various above-mentioned examinations after water-cooling at 40 ** was manufactured.

(5) When the method which cut out the predetermined specimen from the sheet-shaped slush molding object acquired above (4) (sampling), and described above a sex with a crack-proof, abrasion resistance, rubber elasticity (permanent set), pliability (hardness), and tensile strength measured or estimated, it was as being shown in the following Table 1 and 2.

[0080]

[Table 1]

| | 実施例 1 | 実施例 2 | 実施例 3 | 実施例 4 |
|---|-------|-------|-------|-------|
| 【粉末状重合体組成物の組成(質量部)】 | | | | |
| 付加重合系ブロック共重合体(I-1) | 100 | 100 | 100 | 0 |
| 付加重合系ブロック共重合体(I-2) | 0 | 0 | 0 | 100 |
| ポリウレタン系ブロック共重合体(II) | 100 | 70 | 70 | 100 |
| 熱可塑性ポリウレタンエラストマー(III) | 300 | 150 | 100 | 300 |
| 軟化剤(IV) | 50 | 100 | 200 | 50 |
| 粉末状重合体組成物の平均粒径(μm) | 410 | 340 | 315 | 355 |
| 粉末状重合体組成物のMFR ($\text{g}/10\text{分}$) | 40 | 80 | >100 | 30 |
| 粉末状重合体組成物のスラッシュ成形性 | ○ | ○ | ◎ | ○ |
| 粉末状重合体組成物の分散粒子の長径(μm) | 2 | 3 | 3 | 2 |
| 【成形体の物性】 | | | | |
| 耐傷つき性(荷重)(MPa) | 0.098 | 0.048 | 0.049 | 0.095 |
| 耐摩耗性(摩耗量)(cm^3) | 0.008 | 0.031 | 0.050 | 0.035 |
| ゴム弾性(永久伸び)(%) | 9 | 10 | 8 | 10 |
| 柔軟性(硬度) | 70 | 53 | 35 | 72 |
| 引張強度(MPa) | 11.4 | 9.4 | 6.5 | 10.8 |

[0081]

[Table 2]

| | 比較例 1 | 比較例 2 | 比較例 3 |
|---|-------|-------|-------|
| 【粉末状重合体組成物の組成(質量部)】 | | | |
| 付加重合系ブロック共重合体(I-1) | 100 | 100 | 100 |
| 付加重合系ブロック共重合体(I-2) | 0 | 0 | 0 |
| ポリウレタン系ブロック共重合体(II) | 0 | 100 | 70 |
| 熱可塑性ポリウレタンエラストマー(III) | 100 | 600 | 150 |
| 軟化剤(IV) | 100 | 50 | 100 |
| 粉末状重合体組成物の平均粒径(μm) | 340 | 355 | 910 |
| 粉末状重合体組成物のMFR ($\text{g}/10\text{分}$) | 50 | >100 | >100 |
| 粉末状重合体組成物のスラッシュ成形性 | △ | ○ | × |
| 粉末状重合体組成物の分散粒子の長径(μm) | 15 | 3 | 3 |
| 【成形体の物性】 | | | |
| 耐傷つき性(荷重)(MPa) | 0.010 | 0.115 | 測定不可 |
| 耐摩耗性(摩耗量)(cm^3) | 0.430 | 0.003 | 測定不可 |
| ゴム弾性(永久伸び)(%) | 13 | 30 | 破断 |
| 柔軟性(硬度) | 65 | 87 | 53 |
| 引張強度(MPa) | 4.5 | 12.5 | 1.2 |

[0082] So that it may see to the result of above-mentioned Table 1 and 2 the powdered polymer composition of Examples 1-4, Addition condensation system block copolymer (I), polyurethane system block copolymer (II), Thermoplastic polyurethane elastomer (III) and softener (IV) are contained in a specific quantity specified by this invention, and when the mean particle diameter is 800 micrometers or less, the MFR value is highly excellent in the moldability. And the Plastic solid acquired from the powdered polymer composition of Examples 1-4 was excellent in a sex with a crack-proof, and abrasion resistance, and also is provided with rubber elasticity, pliability, and the dynamic performance with sufficient balance. The powdered polymer composition of the

comparative example 1 by not containing polyurethane system block copolymer (II) to it, When the content of thermoplastic polyurethane elastomer (III) separates from the range specified by this invention, the powdered polymer composition of the comparative example 2, By having separated from the range which the mean particle diameter specifies by this invention, a sex with a crack-proof, abrasion resistance, or tensile strength is inferior in the powdered polymer composition of the comparative example 3 compared with the Plastic solid acquired from the powdered polymer composition of Examples 1-4.

[0083]

[Effect of the Invention]The powdered polymer composition of this invention is excellent in the moldability (especially melting mobility).

It can use effective in the forming technique using powdered resin, such as slush molding, compression molding, rotational casting, extrusion molding, and calender molding, and can use for various powder coating technology good further.

Especially when it uses for slush molding, the Plastic solid which has unevenness (pattern) and the complicated shape of the shape of leather JIBO or the shape of a stitch can be manufactured smoothly. The Plastic solid and coat (coated product) which are obtained using the powdered polymer composition of this invention are excellent in a sex with a crack-proof, and abrasion resistance, and even if it receives friction and contact by high frequency, it is hard to be damaged, and moreover, they are excellent in pliability, the low-temperature characteristic, rubber elasticity, a hand, and appearance. Since halogen is not contained in the polymer component or softener which the powdered polymer composition of this invention does not contain the plasticizer in which doubt of environmental hormone and carcinogenicity are suspected, and constitute the powdered polymer composition, There are no worries about generating of the dioxin by incineration, environmental hormone, carcinogenicity, etc., and it excels in safety.

[Translation done.]